

# Carbonation Resistance of Concrete with Fly Ash as Fine Aggregate

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**Abstract.** In order to investigate the carbonation resistance of concrete with fly ash as fine aggregate (CFA), the rapid carbonation test was conducted to explore the influence of the curing age, water-to-cement (w/c) ratio, fly ash replacement rate and the activator on the carbonation depth. The experimental results show that prolonging the curing time is beneficial to improving the carbonation resistance of the CFA. The carbonation depth of the CFA correlates positively with the w/c ratio. With an increase in the fly ash replacement rate and w/c ratio, the carbonation resistance of the CFA increases to a remarkable extent. After 28 days of standard maintenance of the CFA, the compactness of the CFA is boosted due to the pozzolanic effect of the fly ash, and its carbonation resistance is enhanced compared to that of ordinary concrete. In addition, the incorporation of the activator marginally contributes to the improvement of the carbonation resistance of the CFA.

## 1. Introduction

China is the world's largest coal consumer and fly ash is the main bulk industrial waste of coal [1]. As energy demands have continued to increase, by the end of 2016, the stock of fly ash has reached three billion tons in China. This substantial accumulation of fly ash not only occupies a large amount of farmland, but also pollutes the environment, destroys the ecological balance, and causes serious environmental and social problems. At the same time, river sand is an important ingredient in producing concrete, and excessive river sand has caused some geological disasters, such as the collapse of river banks, and river bridges being scrapped. Under this scenario, researchers have proposed to blend fly ash into concrete as a replacement for fine aggregate, thus turning the waste into something valuable[2-8]. Besides, the compressive strength, flexural strength, splitting resistance, and wear resistance of the concrete can also be improved over those of ordinary concrete [7-8]. At present, the research on CFA mainly focuses on its strength, blending, and shrinkage properties, and lacks systematic research on the carbonation performance of CFA. Carbonation is an important prerequisite for steel corrosion; corrosion causes a protective layer to separate, causing cracks along the steel bars[9-10]. This will further result in a reduction in the bond strength and effective area of the steel bar, seriously threatening the bearing capacity and durability of the reinforced concrete structure. In order to investigate the durability of the CFA, the rapid carbonation test is conducted to explore the influence of the curing age, water-to-cement (w/c) ratio, fly ash replacement rate and the activator.

The research results provide a reference for further research on the carbonation of CFA in complex environments.

## 2. Materials and experiments

### 2.1. Materials and experiments

The cement was P·O 42.5R cement produced by Ningxia Saima Cement Plant. The fly ash was Glass III fly ash (equivalent to Class C fly ash) from Xixia Thermal Power Plant, with density of 2.058 g/cm<sup>3</sup> and ignition loss of 5.74%, and the chemical composition was shown in Table 1. The fine aggregate was natural river sand. The fineness modulus of the river sand was tested to be 2.71, which was medium sand. The coarse aggregate adopts the continuous graded gravel with particle size of 5~31.5 mm, mud content of 0.6% and crushing index of 10.2%. A powdery naphthalene-type superplasticizer that was suitable for CFA was used to ensure a desirable slump value, and the mixing amount was 2%-3.5% of the mass of the cement in the mixture. The water was tap water.

**Table 1.** Chemical composition of fly ash (%)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
50.35	29.65	5.85	6.61	1.83	1.72	1.13	0.335	2.11

### 2.2. Mixture Proportion

According to the experimental design, the w/c ratio of concrete was determined as 0.60, 0.55, and 0.50, The equivalent volume replacement rate of fly ash were 0% and 15%. The mix design is shown in Table 2. Formula (1) represents the replacement of 15% fine aggregate with an equal volume of fly ash:

$$M_{FA} = \frac{M_S \cdot 15 \cdot \rho_{FA}}{\rho_S} \quad (1)$$

where  $\rho^S$  and  $\rho^{FA}$  are the densities of fine aggregate and fly ash, respectively;  $M_S$  and  $M_{FA}$  are unit consumptions of fine aggregate and fly ash, respectively;

**Table 2.** Mixture proportions for a cubic-meter of concrete

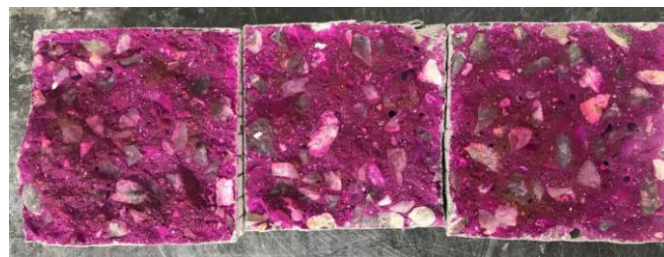
Water to cement ratio	Fly ash replacement ratio: %	Water: kg/m <sup>3</sup>	Cement: kg/m <sup>3</sup>	Fly ash: kg/m <sup>3</sup>	Sand: kg/m <sup>3</sup>	Gravel: kg/m <sup>3</sup>	Superplasticizer : kg/m <sup>3</sup>
0.60	0	185.3	308.8	0	840.3	1027.0	6.2
0.60	15	185.3	308.8	96.4	743.9	1027.0	6.2
0.55	15	185.3	336.9	96.0	590.0	1030.5	6.7
0.50	15	185.3	370.6	96.1	563.2	1030.1	9.3

### 2.3. Experimental method

The prism test block of 100 mm×100 mm×400 mm was used, with three blocks in one group. The experimental procedures comply with the rapid carbonation method in accordance with the Chinese standard GB/T 50082-2009. The specific procedures were as follows. The test specimens were placed in a standard maintenance room with curing age of 3 d and 28 d, respectively. Two days before the test, the test specimens were taken out and placed in a 60°C oven for 48 h, and then placed in a carbonation box, as shown in Figure 1. When the test specimens were carbonized to 3 , 7 , 14 and 28 d, the prism specimens were taken out and the carbonation depth was measured. A rock cutter was used to break the shape and brush the powder on the section, and the phenolphthalein solution was sprayed. The region with purple color was considered as the carbonated zone and if it did not change color, it was carbonized zone, as shown in Figure 2. The carbonation depth of each point was measured every 10 mm using a digital vernier caliper with accuracy of 0.1 mm, and the average value was taken as the carbonation depth of the test specimen at the carbonation time. Table 3 shows the results of the rapid carbonation test of CFA.



**Figure 1.** Carbonation testing machine.



**Figure 2.** Carbonation depth measurement

**Table 3.** Carbonation depth of CFA

Ingredients	Fly ash replacement ratio: %	Water-to-cement ratio	Carbonation depth (mm)			
			3d	7d	14d	28d

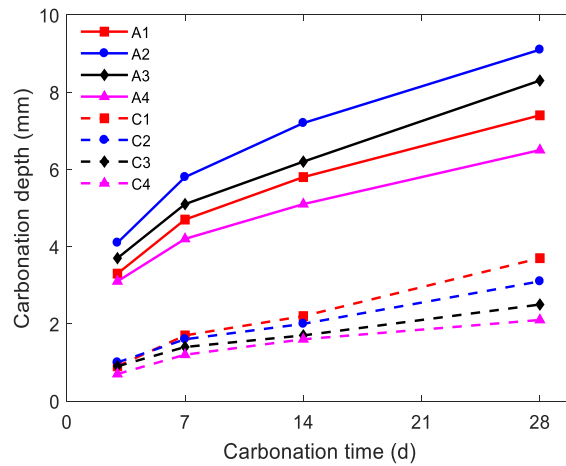
A1	0	0.60	3.3	4.7	5.8	7.4
A2	15	0.60	4.1	5.8	7.2	9.1
A3	15	0.55	3.7	5.1	6.2	8.3
A4	15	0.50	3.1	4.2	5.1	6.5
C1	0	0.60	0.9	1.7	2.2	3.7
C2	15	0.60	1.0	1.6	2.0	3.1
C3	15	0.55	0.9	1.4	1.7	2.5
C4	15	0.50	0.7	1.2	1.6	2.1
C4-1	15	0.50	0.6	1.0	1.2	1.5

**Note:** The standard curing age number is 3d for class A and 28d for class C. The C4-1 is doped with 1% activator (anhydrous sodium sulfate)

### 3. Results and discussion

#### 3.1. Influence of curing age on carbonation depth

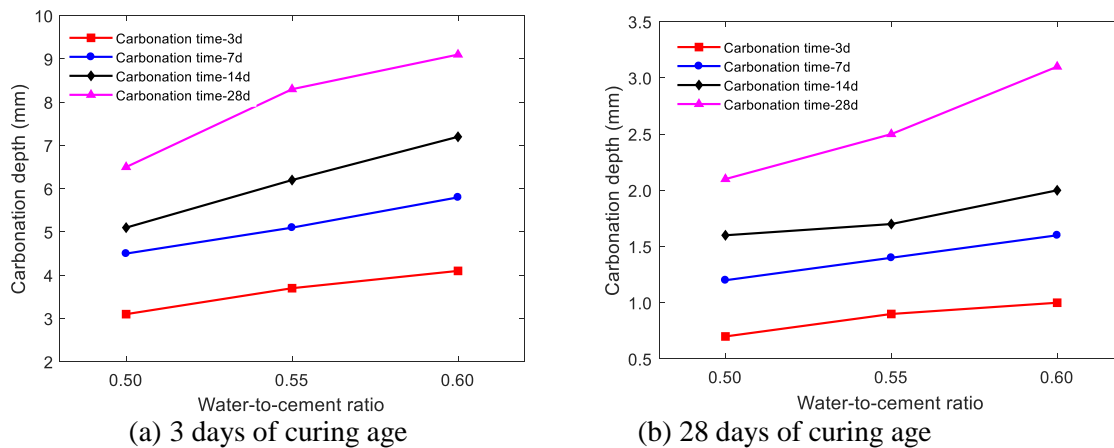
The rapid carbonation experiment of CFA was carried out according to the mixture in Table 2. The relationship between the curing age and the carbonation depth is shown in Figure 3. It can be seen from Figure 3 that when the concrete is not sufficiently cured, that is, the standard curing age of 3 d, the carbonation of CFA became more serious as the carbonation time increased. Under the same w/c ratio (0.6), the carbonation of CFA was rapid while its carbonation resistance was weak. The main reason was that when CFA was not sufficiently cured, the cement hydration would not be complete; the initial holes were massive and large. As a result, the internal structure of CFA was not compact, and CO<sub>2</sub> could easily entered CFA, increasing the carbonation speed[11-12]. Although the products such as C-S-H gel formed by the pozzolanic reaction of the fly ash in the later stage were favorable for refining the pore structure, the large pores caused by insufficient early curing were difficult to be filled, and the channels for high concentration of CO<sub>2</sub> entering were still there [13]. With the increase of carbonation age, the lower the Ca(OH)<sub>2</sub> content in CFA, the more easily the CFA was carbonized and the carbonation developed rapidly. For the curing time of 28 d, the w/c ratio was 0.6, the fly ash replacement rate was 0% and 15%. When CFA was cured for 28 d (i.e., sufficient curing), the carbonation depth was significantly lower than that of the concrete cured for 3 d (under-maintenance), with the carbonation depth reducing from 7.4 mm and 9.1 mm to 3.7 mm and 3.1 mm, respectively.



**Figure 3.** Influence of curing age on carbonation depth

### 3.2. Influence of w/c ratio on carbonation depth

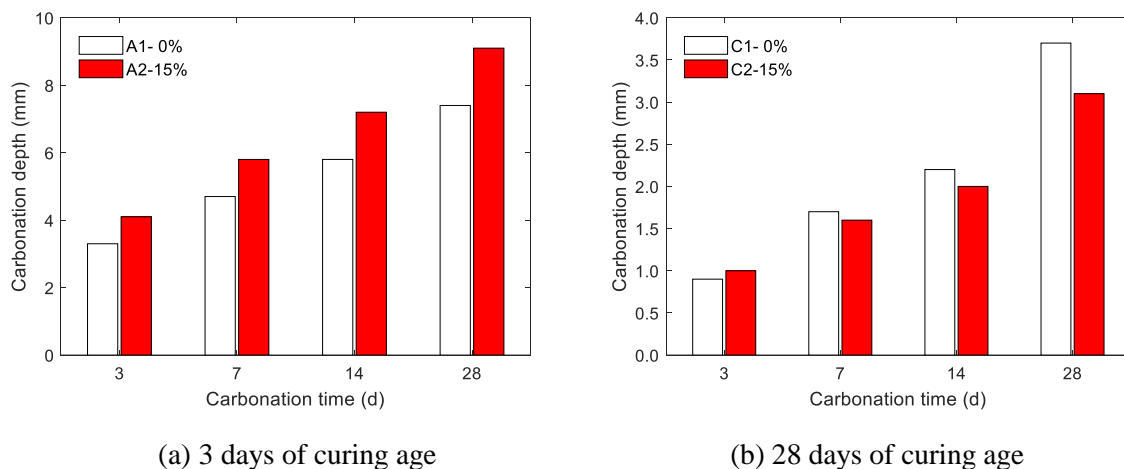
It is well known that the w/c ratio is one of the important factors affecting the carbonation resistance of concrete [14-15]. The value of w/c ratio determines the internal microstructure and macroscopic properties of concrete. In order to investigate the effect of w/c ratio on the carbonation of CFA, the water-to-cement ratio are the A2~A4, C2~C4 series shown in Table 3. The relationship between w/c ratio and carbonation depth is shown in Figure 4. It can be seen from Figure 4 that the carbonation depth of CFA is positively correlated with the w/c ratio. When the carbonation time did not exceed 7 d, the effect of w/c ratio was not obvious. But when carbonized to 28 d, the carbonation depth increased obviously with the increase of w/c ratio. The main reason was that the larger the w/c ratio, the more pores in the concrete, the more easily the  $\text{CO}_2$  would diffuse [16]. In addition, as the  $\text{Ca}^{2+}$  concentration in the concrete decreased, in order to maintain the balance,  $\text{Ca}(\text{OH})_2$  would continue to dissolve, resulting in a reduction in the liquid alkalinity and alkali reserve. When the pH value or  $\text{Ca}(\text{OH})_2$  decreased to a certain level, the other calcium-containing hydration products would decompose and carbonize, resulting in an increase in the carbonation value of the concrete and a decrease in the carbonation resistance of CFA.



**Figure 4.** Influence of w/c ratio on carbonation depth. (a) 3d of curing age and (b) 28d of curing age

### 3.3. Influence of fly ash replacement rate on carbonation depth

Figure 5 shows the effect of the fly ash replacement rate on the carbonation depth of the concrete. As can be seen from Figure 5a, when the concrete was cured for 3 d, the carbonation depth of CFA under different carbonation times was larger than that of ordinary concrete, and the carbonation was accelerated in the later stage. This was because when the curing was insufficient; the hydration of the fly ash was insufficient, resulting in a significant increase in the porosity, number of coarser pores and air permeability of the researched concrete than ordinary concrete. Therefore, the penetration and diffusion rate of  $\text{CO}_2$  in the air was accelerated, and the carbonation depth at each curing age was also increased. It can be found from Figure 5b that when the concrete was cured for 28 d, the carbonation depth of CFA was slightly larger than that of ordinary concrete except for the carbonation time of 3 d, which might be due to experimental error. By contrast, the carbonation depth of CFA under other carbon age was smaller than that of ordinary concrete, and the difference became more obvious with the increase of carbonation time. This was because in the concrete where fly ash replaced fine aggregate, the amount of cement in the concrete was not reduced compared with the traditional fly ash instead of cement. In addition, with the progress of cement hydration, the hydration product  $\text{Ca}(\text{OH})_2$  increased, which in turn stimulated the participation of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the fly ash, and the gel products such as CSH and CAH were filled into the pores of the interfacial transition zone[17-18]. This had improved the compactness of the concrete and thus improved the carbonation resistance of the concrete to some extent.

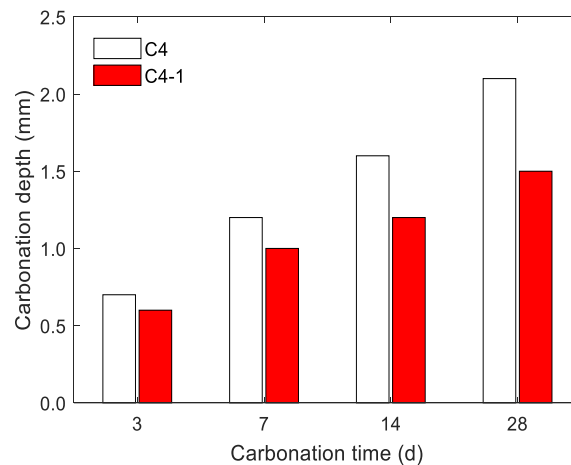


**Figure 5.** Influence of fly ash replacement rate on carbonation depth. (a) 3d of curing age and (b) 28d of curing age

### 3.4. Influence of activator on carbonation depth

Since the low w/c ratio is beneficial to the carbonation resistance of CFA, the C4 sample was separately doped with 1% anhydrous sodium sulfate activator (labeled as C4-1), followed by the rapid carbonation test with standard curing time of 28 d. The results are shown in Table 4 and Figure 6. For the same carbonation age, the carbonation depth of CFA doped with the activator was slightly reduced; the carbonation depth of the C4 group for rapid carbonation of 28 d was 2.1 mm; the carbonation depth of the C4-1 group for rapid carbonation of 28 d was 1.5 mm, indicating that the activator could slightly improve the carbonation resistance of CFA. In actual engineering, due to the low concentration of  $\text{CO}_2$  in the atmosphere, the carbonation process is very slow[19]. When the

curing is sufficient, the pozzolanic reaction of the fly ash in the concrete continues, the internal compactness of the concrete is continuously increased, the porosity is reduced, and the carbonation speed is also reduced. Therefore, the carbonation resistance of CFA is continuously enhanced.



**Figure 6.** Influence of activator on carbonation depth

#### 4. Conclusion

- a) The curing system has a great influence on the carbonation resistance of concrete, and prolonging the curing time is beneficial to improving the carbonation resistance of concrete.
- b) The carbonation depth of CFA is positively correlated with the w/c ratio. The carbonation depth increases as the w/c ratio increases.
- c) When the curing is insufficient, the carbonation is accelerated in the later stage. Compared with ordinary concrete, the carbonation of the CFA is greater. When the curing is sufficient the pozzolanic effect of fly ash improves the compactness of concrete, thus improving the carbonation resistance of the CFA to some extent.
- d) The incorporation of the activator marginally contributes to the improvement of the carbonation resistance of the CFA.

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